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Conversion of Xylose into D-Xylitol using Catalytic Transfer Hydrogenation with Formic Acid as H-Donor

Danuta Joanna Aigner,[a,*] Lena Hinterholzer,[a, c] Lukas Almhofer,[a] Robert H. Bischof,[b] and Tanja Wrodnigg[c]

D-Xylitol, a biomass-derived sweetener, is increasingly used in cosmetics and pharmaceutical products. The raw material for D-xylitol production, D-xylose, is easily accessible from dissolving pulp production. D-xylitol production involves the heterogeneously catalyzed hydrogenation of D-xylose; this process is energy intensive, as the use of H_2 requires high pressure and temperature. This work examined catalytic transfer hydrogenation for xylose conversion into xylitol. Formic acid (FA) was used to replace H_2 as the H-donor, as it is easily available, inexpensive, may be obtained from renewable sources, and it avoids the risks associated with the use of high-pressure inflammable gas. A variety of commercially available catalysts were screened to reveal the one enabling the highest yield. The experiments were performed at 40, 80, and 140 °C, with pure xylose as a model compound. Triethylamine (Et_3N) was added to ensure sufficient conversion rates. Based on the preliminary studies an experimental design was created (Design Expert®), including the two best performing catalysts Ru/Al_2O_3 and Ru/C, to investigate the influence of temperature and H-donor and base concentration on xylitol yield. Ru/C resulted in maximum D-xylitol yield of 73.2 % at 100 °C, FA to D-xylose ratio 5:1 and Et_3N to FA ratio 0.4.

*Contact information: a: Kompetenzzentrum Holz GmbH, Altenberger Straße 69, 4040 Linz, Austria; b: Lenzing AG, Werkstraße 2, 4860 Lenzing, Austria; c: IBioSys Institute of Chemistry and Technology of Biobased Systems, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria; * Corresponding author: d.aigner@wood-kplus.at*

INTRODUCTION

Bio-based alternatives must be substituted for as many as possible resources of fossil origin as a means to reach the climate goals and to preserve the quality of life on Earth for future generations. Many potential biomass-originating chemicals are still underexploited, due to higher resulting production and purification costs compared to their petrochemical counterparts. This might change with the increase of CO_2-pricing, thereby demanding low carbon emitting technologies. However, ongoing development of innovative production processes and sustainable resource management still have to be done to guarantee the most efficient use of the raw materials (Dean *et al*. 2005).

Lignocellulosic biomass is an ideal source for the production of chemicals and raw materials, as it lacks competition with the food industry, is inexpensive, and may be processed into a wide variety of products (Clements and Van Dyne 2005). Cellulose, hemicellulose and lignin, the main components of lignocellulosic feedstock, differ in

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chemical structure and properties, leading to manifold potential applications. Looking at textile fibers (viscose or lyocell) as the intended product, dissolving pulp with highest possible cellulose content is manufactured as a basic material, with the majority of lignin and hemicellulose remaining in the cooking liquor after the initial pulping step. The high energy content of the residual lignin, due to the aromatic structure, makes it well suited for energy generation, increasing the process sustainability. Hemicellulose, on the other hand, especially when originated from hardwood, is an excellent source of xylose and may be further processed into xylitol, which is in strong demand on the global market (Bozell and Petersen 2010; Felipe Hernández-Pérez *et al.* 2019; Delgado Arcaño *et al.* 2020). The content of hemicellulose in hardwood is 25 to 35%, dependent on species. Thus, it has great potential for valuable by-products. The worldwide demand for wood originated textile fibers is expected to constantly increase, due to population growth and limited availability of cotton cultivation areas. In parallel, the availability of hemicellulose as a renewable raw material will continue to grow (Gschwandtner 2022).

Besides wood pulp production effluents, xylose containing hemicellulose is present in several feedstocks (straw, reeds, grass, wood, paper waste, *etc.*). However, using effluents originating from an established process carried out on a large scale guarantees a constant supply of the required raw material and results in a significantly reduced environmental impact compared to the competitive biomass hydrolysis process. After xylose separation from the acidic pulping liquor, it is converted to xylitol by catalytic hydrogenation (Heikki *et al.* 1999; Delgado Arcaño *et al.* 2020). Although the production process is well-established, it involves several operational and economical drawbacks, due to laborious and energy-intensive purification and H_2-containing steps (Melaja *et al.* 1977). The hydrogenation step is typically carried out in batch reactors at 80 to 140 °C and pressures up to 50 bar H_2. The reaction conditions require cost-intensive infrastructure due to the hazard of H_2 handling. Further, highly selective metal catalysts have to be used, to prevent side reactions and guarantee maximum xylitol yield, implying intensive xylose purification steps. Traditionally, Raney nickel (<0.1 mm) is used as catalyst. However, this catalyst has some disadvantages in batch production (toxicity, deactivation due to leaching and instability, formation of by-products such as aldonic acids). Considering the fact that xylitol is mainly used in food industry and cosmetics, catalyst toxicity presents a considerable risk and entails cost-intensive purification steps such as ion exchange, filtration, and crystallization. In recent years, a variety of noble metal based (Pt, Pd, Ru) catalysts have been developed, showing good activities and selectivity and with the potential to replace Raney nickel (Sánchez-Bastardo *et al.* 2018). The catalytic activity of the noble metals decreases in the order Ru>Ni>Rh>Pd, with Ru catalysts showing high activities especially in the neutral and basic range.

Ru has been preferred due to its ability to effectively hydrogenate ketones into alcohols under relatively mild reaction conditions in aqueous solutions (Seretis *et al.* 2020). As is the case for almost every catalyst, some limitations due to undesired reactions and inactivation may occur. Reduced catalyst performance caused by CO adsorption during CO_2 hydrogenation was reported by Xu *et al.* (2020). A slightly reduced conversion velocity was observed when Ru/C was reused up to 5 times in hydrogenation of 1-methylpyrrole, due to nitrogen adsorption. Surprisingly, during the first reuse, significantly increased activity at room temperature was detected, compared to the fresh catalyst. The authors assigned the phenomenon to the removal of an initial RuO_2 layer (Hegedűs *et al.* 2018). Especially when using Al_2O_3 as a support, the presence of chlorine significantly

reduces the amount of the adsorbed hydrogen, due to selective site blocking. Therefore, one should keep that in mind as well (Lin *et al.* 2011).

Another interesting issue was demonstrated by Hua *et al.* (2021). In their work, the influence of the catalyst supporting material on the product composition of 2,5-hexanedione hydrogenation was investigated. Dependent on the support structure, different reaction routes were favored, resulting in different products, both using Ru as a catalyst (Hua *et al.* 2021).

Attempts were recently made to reduce the resources and energy consumption within the xylitol production process. In the one-pot method proposed by Yi and Zhang (2012), hydrolysis and the subsequent hydrogenation of xylose-containing hemicellulose is completed within a single reaction step. The reaction requires the addition of an acid and a metal catalyst. The absence of acid in the reaction mixture led to significantly reduced xylitol yields.

The challenging handling of the easily diffusing and inflammable hydrogen gas, as well as the fact that it is mostly generated from fossil raw materials, provide reasons for its replacement by less problematic hydrogenating agents, which is a promising opportunity to create greener, more sustainable, efficient, and safe process conditions. Catalytic transfer hydrogenation (CTH) with low molecular mass organic molecules (*e.g.*, alcohols or acids), especially if originating from bio-based sources, are particularly suitable for that purpose. Espro *et al.* (2018) described the use of short-chain alcohols and formic acid as appropriate H-donors in transfer hydrogenation reactions. The possibility of transfer hydrogenation of glucose into sorbitol, involving biomass-derived alcohols was demonstrated by Garcia *et al.* (2019, 2021). However, the problematic Ni-containing catalysts were used in the experiments. An advancement in the reduction of different functional organic compounds such as nitroarenes, olefins, and carbonyl compounds was recently presented by Goyal *et al.* (2023). In their work, methanol was used as a hydrogen source in the presence of a commercially available Pt/C catalyst.

Besides the alcohols, formic acid has been successfully applied as an H-donor in CTH for the reduction of sugar derivatives or various biomass-derived molecules (Jicsinszky and Iványi 2001; Wang *et al*. 2021; Sultana *et al*. 2023). The reactions require relatively mild conditions and exclude the risk of handling hydrogen gas. Commercial hydrogenation technology usually requires large investments in hydrogen gas infrastructure and safety equipment. On this account formic acid displays high potential for future applications, especially for small decentralized bio-refinery approaches. Formic acid is formed during biomass conversion, *e.g*. in the course of kraft pulping, the formation of furfural or catalytic biomass oxidation (Reichert and Albert 2017; Bulushev and Ross 2018; Preuster and Albert 2018; Valentini *et al*. 2019). Formic acid can also be produced from CO_2, which makes it a potentially carbon neutral reactant. However, the use of formic acid for transfer hydrogenation still requires metal catalysts. Noble metal catalysts, such as Ru, Au, Pd, and Pt, are preferentially used, due to their high activity in hydrogenation of different functional groups (Gilkey and Xu 2016).

In the literature, a combination of formic acid (FA) with organic/inorganic bases was shown to increase the efficiency of FA in CTH reactions (Gilkey and Xu 2016). In practice, it results in an increase of the complexity and costs of the process. Low-molecular-weight amines, such as triethylamine (Et_3N), are often chosen, whereby the molar ratio of FA/Et_3N has a considerable effect on the performance of the reaction (Zhou *et al*. 2012). Adding Et_3N favors the formation of $[NEt_3H][CO_2H]$ and enhances the reactivity of formate over the metal center. CO_2 can then easily be liberated from the

formate ion leaving the hydride ion on the surface of the metal. Subsequently, these active metal hydrides or dihydrogen complexes can hydrogenate the substrates (Nie *et al.* 2021). In Fig. 1, a reaction scheme of catalytic transfer hydrogenation of xylose using formic acid as the H-donor with Ru/C as a catalyst is shown.

Design of experiments (DoE) is an established tool to generate information with minimized experimental effort and is successfully applied in several research fields (Bowden *et al.* 2019; Almhofer *et al.* 2023a). Appropriate software supports the optimization of reaction conditions and statistical data evaluation in systems containing multiple variables and facilitates a graphical presentation of the results. A strategically planned and executed experiment can provide a great deal of information about the effects of one or more factors on a response variable. Therefore, it was an ideal solution for the optimization of the CTH reaction conditions to obtain the highest xylitol yield.

A more than fortyfold increase in xylitol production in the recent forty years illustrates the growing demand for the low-calorie sucrose substitute (Delgado Arcaño *et al.* 2020). Although D-xylitol is derived from cheap and abundant lignocellulosic biomass, its production process is expensive due to energy-intensive steps and the need for H_2 as the hydrogenation agent.

Herein, an alternative method of D-xylitol production *via* catalytic transfer hydrogenation (CTH) of xylose without the use of an undesired Ni-catalyst was investigated.
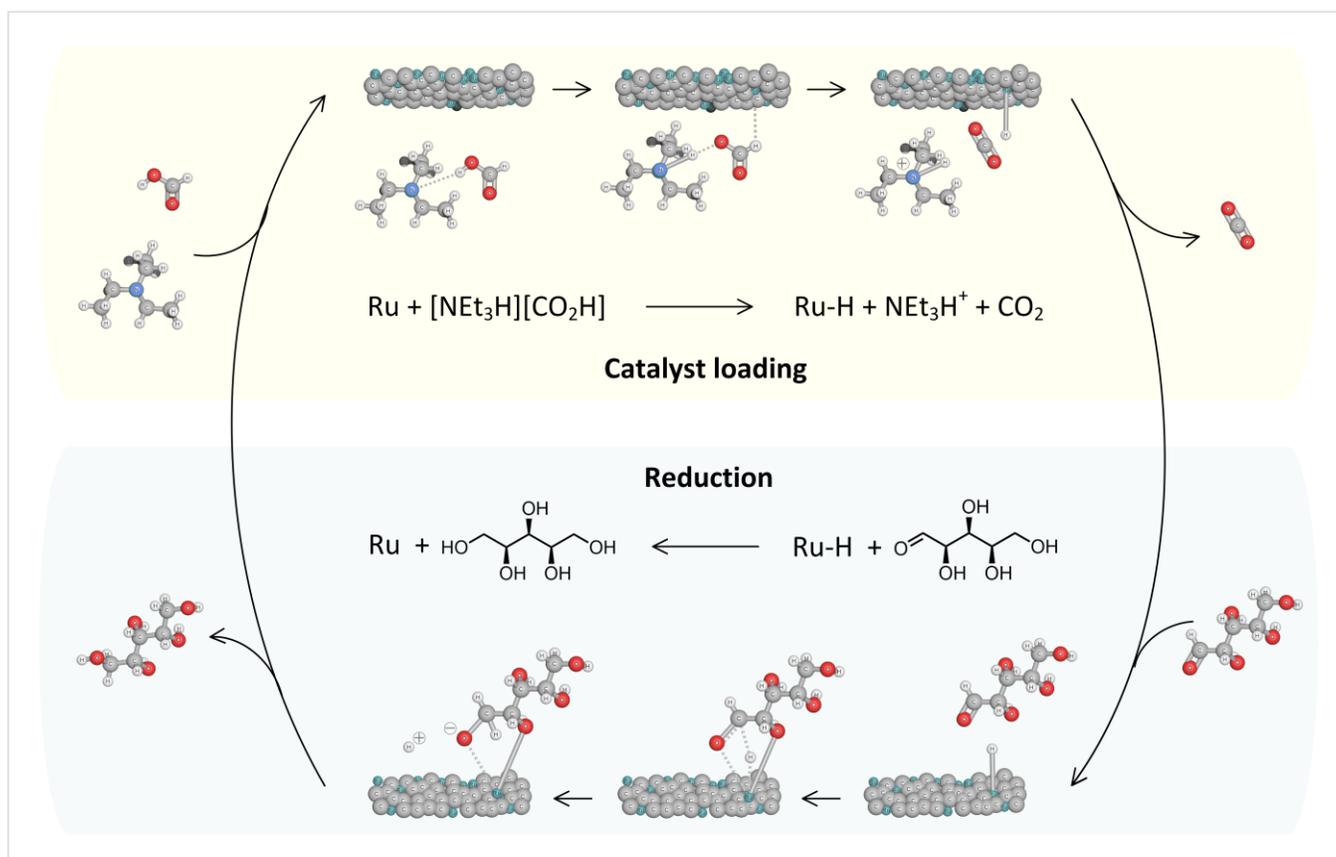

Fig. 1. Reaction scheme of catalytical transfer hydrogenation of xylose using formic acid as an H-donor and Ru/C catalyst

EXPERIMENTAL

Materials

The chemicals used in the catalytic transfer hydrogenation experiments are listed in Table 1.

Table 1. Chemicals Used in the HTC Experiments

Chemical	Abbreviation	Supplier	Purity [%]
D-Xylose	Xyl	Tokyo Chemical Industry (Tokyo, Japan)	> 98
Formic acid	FA	Sigma Aldrich	99
Triethylamine	Et$_3$N	Merck	99

Ru/HTC and Ru/Al$_2$O$_3$ catalysts were kindly provided by Heraeus (Hanau, Germany). All the other catalysts tested were commercially available and were purchased from Thermo scientific and Sigma Aldrich. A compilation of the catalysts used is displayed in Table 2.

Chemicals used for the analyses described in the corresponding section were of analytical grade. More detailed information may be found in the referred publications.

Design Expert® Software (version 13.0.4.0, Stat-Ease Inc., Minneapolis, MN, USA) was used to design the optimization experiment, statistical analysis, and the resulting model graph creation.

Table 2. Catalysts Used in the Experiments and the Related Metal Content

Catalyst	Metal Loading	Supplier
Ru/C	5 % Ru on activated carbon (50 % wet)	Thermo scientific
Ru/Al$_2$O$_3$	5 % Ru on aluminia powder	Thermo scientific
Pd/C	5 % Pd on activated carbon (50 % wet)	Thermo scientific
Pd/Al$_2$O$_3$	10 % Pd on aluminia powder	Sigma Aldrich
Ru/HTC	3 % Ru on Hydrotalcite	Heraeus (charge 190754)
Ru/Al$_2$O$_3$	3 % Ru on aluminia powder	Heraeus (charge 190745)

Methods

Analytical methods

Quantification of D-xylose and D-xylitol was done by HPLC (anion exchange chromatography with pulsed amperometric detection) using a Dionex ICS 5000+ system with a Dionex CarboPac SA10 4x50 mm as pre-column and a Dionex CarboPac SA10 4x250 mm separation column (Almhofer *et al*. 2023b).

Xylonic acid concentration was determined by ion exchange chromatography with a Dionex CarboPac SA10 4×50 mm as pre-column and a Dionex CarboPac SA10 4×250 mm column (Wolfsgruber *et al*. 2023).

The furfural and furfuryl alcohol concentrations were quantified with reversed phase HPLC with UV detection using a Thermo BDS Hypersil C8 250 x 4.6 mm 5 μL column, as described by Almhofer *et al*. (2023b). The analysis of formate was performed with anion exchange chromatography with conductivity detection and external calibration. A Dionex IonPac AS11-HC 4x250 mm pre-column and a Dionex IonPac AS11-HC 4x250 mm separation column were used in a system described by Almhofer *et al*. (2023b).

The pH values of the solutions were measured before the CTH experiments using a HI1230 pH electrode connected to a HI83141 pH meter (both Hanna Instruments GmbH, Graz, Austria).

Catalyst screening

The catalyst screening experiments were carried out in 450 mL Parr reactors (Stainless steel/T316) at constant pressure of 5 bar N_2, a temperature of 140 °C, and a constant stirring speed of 320 rpm. The stirring speed was chosen based on preliminary tests in which various catalysts were stirred in the reaction medium at room temperature. Stirring speed was chosen as the minimum speed at which the catalysts were homogeneously suspended. This was visually assessed in a transparent plastic reactor having the same size and geometry as the reaction vessels used in the main experiments. The temperature of 140 °C was chosen based on preliminary tests (data not shown).

To around 30 mL of deionized water in a 100 mL volumetric flask, 1.5 g FA, 0.6 g Et_3N and 5 g D-xylose were added and filled up with deionized water. 50 mL of the obtained reaction mixture was volumetrically transferred to the reactor. The heterogeneous catalyst was added in an amount of 1.5 % w/w to xylose. The reactor was twice evacuated and flushed with N_2 to remove air and the pressure was adjusted to 5 bar. After air removal, the reactor was heated, and the temperature was kept constant for 6 hours. Samples were taken after 3 hours through a cooling coil attached to the bottom drain valve. Before sampling, the coil was purged with double the volume of the sampling system. After the desired reaction time, the reactor was cooled with iced water. The catalyst was filtered off and washed with deionized water. The product solution was stored at 5 °C until analysis.

Optimization of hydrogenation conditions

Experiments involving the two best performing catalysts were designed using Design Expert® Software for the purpose of maximizing the xylitol yield by optimization of the reaction conditions. A Box-Behnken experimental design was suggested by the software to evaluate the influence of three parameters: temperature *T*, formic acid to xylose ratio *FA:Xyl*, and triethylamine to formic acid ratio *Et₃N:FA*. The investigated ranges of *T*, *FA:Xyl*, and *Et₃N:FA* were 70 to 130 °C, 1 to 5, and 0 to 0.4 respectively. The center point (*T* = 100 °C, *FA:Xyl* = 3, and *Et3N:FA* = 0.2) was replicated three times to reveal the reproducibility. Xylose conversion (X_{Xyl}), xylitol yield (Y_{XylOH}), and xylitol selectivity (S_{XylOH}) were chosen as responses. The response data was transformed using the arcsine square root function to limit the results to the physical boundaries of 0 and 1. Design Expert statistical software was used for the analysis of variance (ANOVA) and model evaluation. All CTH experiments were performed similar to catalyst screenings, with a reduced time of 3 h and the conditions given by the experimental design program.

Equations

The equations of xylitol yield *Y* calculation (Eq. 1) and the selectivity of xylose conversion into xylitol *S* (Eq. 2) were as follows:

$$Y(Xylitol) = \frac{\frac{C_t(Xylitol)}{M(Xylitol)}}{\frac{C_0(Xylose)}{M(Xylose)}} \tag{1}$$

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$$S(Xylitol) = \frac{\frac{c_t(Xylitol)}{M(Xylitol)}}{\frac{c_0(Xylose)-c_t(Xylose)}{M(Xylose)}} \tag{2}$$

where c_t is the concentration after the reaction (gL^{-1}); c_0 is the initial concentration (gL^{-1}), and M is the molar mass of the component (gmol^{-1}).

RESULTS AND DISCUSSION

Preliminary Catalyst Screening

Six commercially available Ru and Pd catalysts on various support materials were screened for their ability to convert xylose into xylitol *via* CTH using formic acid as an H-donor. Concentrations of the reactants and additives were chosen similar to those typically reported in the literature for analogous CTH reactions (Jicsinszky and Iványi 2001; Sánchez-Bastardo *et al*. 2018; García *et al*. 2021). To assess the catalyst performances, xylitol, residual xylose, and furans (sum of furfural and furfuryl alcohol were analyzed in the reaction solutions. Figure 1 shows the product yields dependent on the catalyst used. Most catalysts produced xylitol in relatively low yields between 4.1% and 22.7%. Interestingly, with the Ru/Al$_2$O$_3$ catalyst from Thermo Scientific a high amount of the original xylose (32.0%) was found, indicating insufficient catalytic activity under the applied conditions. A small amount of xylose (1.4%) was also found in the residual solution of the Pd/Al$_2$O$_3$ catalyst, whereas all other catalysts displayed complete conversion of xylose. The different behavior of both Ru/Al$_2$O$_3$ catalysts should be pointed out. Despite similar composition, a marked difference in the performance and product composition was found. A possible explanation may be the individual particle size and structure of the supporting material or distinct production processes (Jędrzejczyk *et al*. 2020; Vilcocq *et al*. 2021).

Samples taken during the reaction revealed that xylose conversion was completed within 3 h. Therefore, in the subsequent optimization experiments, the reaction time was reduced to prevent xylitol degradation.

Another observed issue was the formic acid consumption rate exceeding the xylose conversion rate. The resulting lack of the hydrogenation agent led to unpredictable side reactions and the additional change of the pH value, favoring various isomerization and degradation reactions of sugars. High pH values ($\geq$ 8) favor isomerization of xylose in xylulose and the formation of xylonic acid (Yadav *et al*. 2012). Therefore, an excess of formic acid was used in the subsequent experiments.

Furfural is known to form during acid catalyzed dehydration of xylose at high temperatures, and furfuryl alcohol may be produced *via* hydrogenation of furfural; hence, their concentrations were determined (Wang *et al*. 2021). Furans were only detected in low amounts (<1 %), except for the Ru/Al$_2$O$_3$ catalyst from Thermo scientific, where 11.9 % furfural and 1.0 % furfuryl alcohol were found. Generally, only a small fraction of the reaction products could be identified with standard methods used in carbohydrate characterization. That fact indicates complex sugar and furan degradation, due to the harsh reaction conditions. This assumption was supported by the dark colors of the residual solutions, which is typical for high molar mass polymerization products. Although the identification of the degradation products would be beneficial and may contribute to the understanding of the reaction, it has not been covered within the current project, as it requires time-consuming method development.
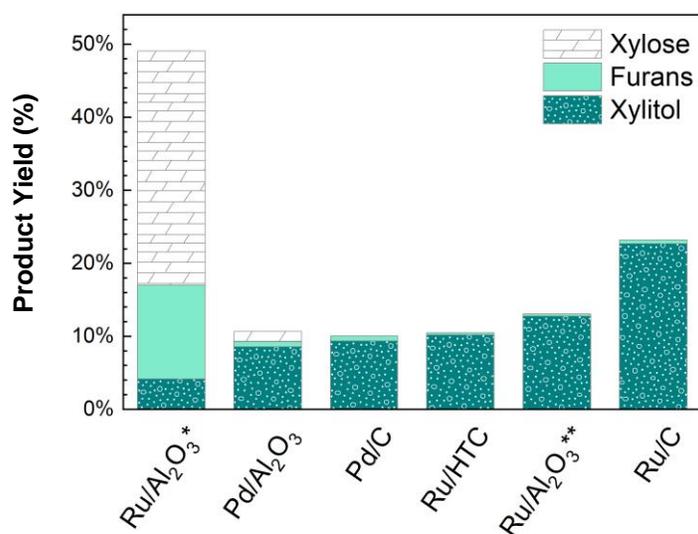
Fig. 2. Yields of xylitol, residual xylose, and furans for six commercially available catalysts in the CTH of xylose using formic acid as H-donor. The catalyst screening was done at a temperature of 140 °C for 6 h, with 50 g L^{-1} xylose, 15 g L^{-1} FA, 6 g L^{-1} Et$_3$N, and a catalyst loading of 1.5 % w/w on xylose.*Thermo scientific **Hereaus

Optimization of Reaction Conditions by DoE

Based on the catalyst screening results, Ru/C (Thermo scientific) and Ru/Al$_2$O$_3$ (Heraeus) were chosen to further investigate the influence of the reaction conditions and to maximize the resulting xylitol yield. An experimental design approach was applied, compiling a set of 15 runs with varying conditions for each catalyst. Temperature (Factor A) was chosen as one of the impact factors, as its reduction generally contributes to the energy balance and concurrently to process efficiency. Further, to minimize undesired side reactions and incomplete xylose conversion due to a reduced hydrogen availability, the concentrations of formic acid and triethylamine were adapted. Enhanced FA/Xyl ratios of 1 to 5 (Factor B) were tested, to ensure a surplus of formic acid during the entire reaction time. Additionally, the influence of different amounts of triethylamine on the expected xylitol yield was investigated as the ratio of formic acid to triethylamine (Factor C:*FA/Et₃N*). Considering the catalyst screening results, the reaction time was reduced to 3 h, to minimize the effect of xylitol degradation occurring at high temperatures and acidic conditions.

In Fig. 2, the response surfaces of the selectivity (a, b) and xylitol yield (c, d) obtained after data evaluation of the Ru/C experiments are shown. Comparing the diagrams, the influence of Et$_3$N addition on both response values was quite pronounced. Without Et$_3$N, the xylitol yields remained low (0 to 3.8 %), whereas at C = 0.4 actual yields of up to 73.2% were obtained with high selectivity and complete xylose conversion (Table 3). At the lowest temperature applied (70 °C) there was no D-xylitol formation. The highest D-xylitol yield and selectivity were obtained in experiment 15 (A = 100 °C, B = 5 eq. FA/Xyl, and C = 0.4).

The results of the experiments with C = 0.2 met the expectations placing in between those of the minimum and maximum C values (graphs not shown). According to the model, a further increase of xylitol yield appears possible with sufficiently high availability of H donor at temperatures slightly below 130 °C.

The reproducibility was calculated from the triplicates of the center point. An average of 56 ± 1.5 % resulted for both xylitol yield and selectivity, as xylose was entirely consumed during the reaction.
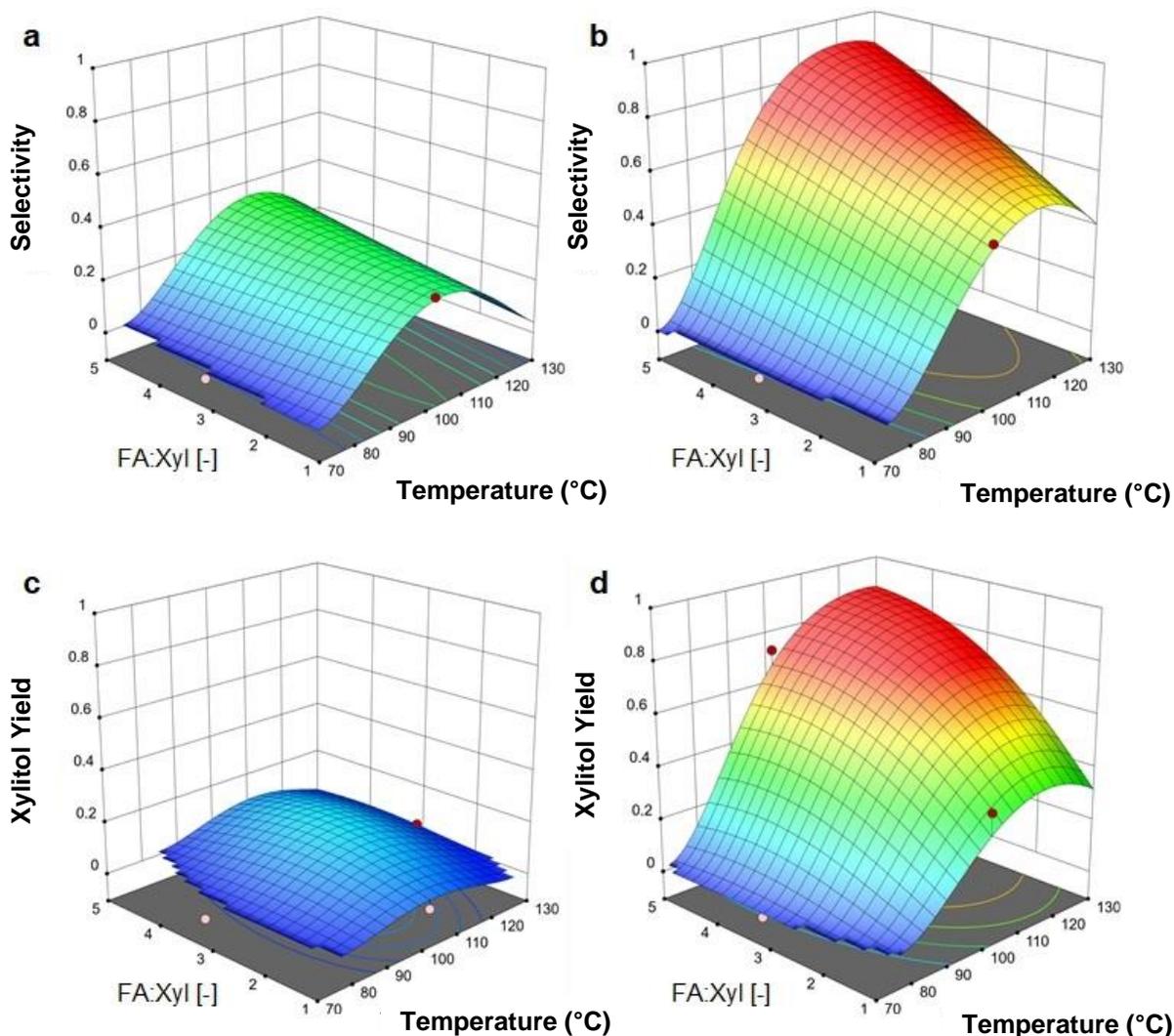

Fig. 3. Response surfaces after DoE using Ru/C as a catalyst. Selectivity and xylitol yield in dependence of Et$_3$N concentration are shown. Figures (a) and (c) illustrate selectivity and xylitol yield without the addition of Et$_3$N, figures (b) and (d) show the results with a Et$_3$N:FA ratio of 0.4.

The model related equations describe the behavior of the response variables within the boundaries and may be used to make predictions about the response for given levels of each factor.

$$ArcSin\sqrt{Y(Xylitol)}$$
$$= -4.973 + 0.097 \times A - 0.095 \times B - 2.378 \times C + 0.002 \times AB$$
$$+ 0.011 \times AC + 0.242 \times BC - 0.0005 \times A^2 - 0.017 \times B^2$$
$$- 6.597 \times C^2$$

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$$ArcSin\sqrt{S(Xylitol)}$$
$$= -4.496 + 0.101 \times A - 0.0171 \times B - 1.480 \times C + 0.002 \times AB$$
$$+ 0.027 \times AC + 0.177 \times BC - 0.0005 \times A^2 - 2.226 \times B^2$$
$$- 6.597 \times C^2$$

Table 3. Parameters of the Experimental Runs and the Resulting Response Values for the CTH with Ru/C

Factors				Response	
Run	A (°C)	B (-)	C (-)	Y(D-xylitol)	S(D-xylitol)
1	130	5	0.2	0.672	0.672
2	130	1	0.2	0.215	0.262
3	100	3	0.2	0.569	0.569
4	100	1	0	0.038	0.304
5	130	3	0	0.038	0.083
6	100	5	0	0.026	0.276
7	100	1	0.4	0.389	0.488
8	100	3	0.2	0.571	0.571
9	70	3	0	0	0
10	70	3	0.4	0	0
11	70	5	0.2	0	0
12	70	1	0.2	0	0
13	100	3	0.2	0.543	0.543
14	130	3	0.4	0.641	0.641
15	100	5	0.4	0.732	0.732
A: temperature; B: *Xyl/FA* ratio; C: *Et₃N/FA* ratio					

The statistical analysis of variance (ANOVA) and diagnostics were performed using Design Expert® software. The results are presented in Table 4. The evaluation of the responses *Y(Xylitol)* in a significant model, A, B, C, AB, AC, BC, A², B² and C² as the significant model terms (p-values < 0.05) and a non-significant Lack of Fit values. Similar results were obtained for *S(Xylitol)* with A, B, C, AB, AC, BC, A² and C² as the significant model terms.

The correlation coefficients between predicted and actual values of D-xylitol yield and selectivity experiments are listed in Table 5. High coefficient of determination indicates a higher reliability of the relationship between predicted and experimentally determined values. If the difference between the predicted and the adjusted R^2 value is less than 0.2, the agreement is reasonable. A larger difference for D-xylitol yield may indicate a large block effect or a problem with the model or the provided data. Consideration must be given to model reduction, response transformation and outlier values. C.V. (coefficient of variation) describes the variation of the data and represents the accuracy and validity of the results. In this case, the C.V. of *S(Xylitol)* is significantly lower, compared to C.V. of *Y(Xylitol)*, indicating less variation of the mean. A signal to noise ratio (Adeq. Precision) > 4 is indicating an adequate signal. The actual values by far exceed that level.

The highest D-xylitol yield of 36.2% was obtained with the Ru/Al_2O_3 catalyst at 130 °C, FA to D-xylose ratio of 3 and base to FA ratio 0.4. Similar to the Ru/C experiments, very low D-xylitol yields were obtained at 70 °C, demonstrating the necessity of Et_3N addition independent of the catalyst used.

Table 4. Analysis of Variance (ANOVA) for Quadratic Model with Arcsin Transformation for Ru/C Catalyst

Parameter	Sum of squares	df	Mean square	F-value	p-value
Y(Xylitol)					
Model	2.10	9	0.234	104.3	0.0002
A-Temperature	0.765	1	0.765	341.57	< 0.0001
B-FA:Xyl	0.080	1	0.080	35.54	0.004
C-Base:FA	0.537	1	0.537	239.8	0.0001
AB	0.057	1	0.057	25.55	0.0072
AC	0.009	1	0.009	4.04	0.1149
BC	0.038	1	0.038	16.78	0.0149
A²	0.523	1	0.523	233.49	0.0001
B²	0.014	1	0.014	6.27	0.0665
C²	0.209	1	0.209	93.22	0.0006
Residual	0.009	4	0.002		
Lack of Fit	0.009	2	0.004	17.72	0.0534
Pure Error	0.001	2	0		
Cor Total	2.11	13			
S(Xylitol)					
Model	2.11	8	0.264	93.97	< 0.0001
A-Temperature	0.925	1	0.925	328.7	< 0.0001
B-FA:Xyl	0.052	1	0.052	18.49	0.0051
C-Base:FA	0.211	1	0.211	75.01	0.0001
AB	0.045	1	0.045	15.88	0.0072
AC	0.101	1	0.101	35.97	0.001
BC	0.020	1	0.020	7.16	0.0367
A²	0.749	1	0.749	266.25	< 0.0001
C²	0.030	1	0.030	10.47	0.0178
Residual	0.017	6	0.003		
Lack of Fit	0.016	4	0.004	17.12	0.0559
Pure Error	0.001	2	0.000		
Cor Total	2.13	14			

Table 5. Results of the Statistical Analysis of the Models for Y(Xylitol) and S(Xylitol) with Ru/C as Catalyst

Parameter	Response	
	Y(Xylitol)	S(Xylitol)
Std. Dev.	0.112	0.053
Mean	0.4776	0.5465
C.V. (%)	23.46	9.7
R²	0.9734	0.9921
Adjusted R²	0.9254	0.9815
Predicted R²	0.5768	0.9205
Adeq Precision	12.6881	26.931

According to the evaluated model, a further increase of xylitol formation appears possible with sufficiently high availability of H donor and temperatures over 130 °C. However, hereby the maximum selectivity at around 110 °C should be considered. Again, the results of the experiments with C = 0.2 were found in between those of the minimum and maximum C values (graphs not shown). The average of xylitol yield calculated form the triplicates at the center point conditions resulted in 15 ± 1.1 %, indicating a good

reproducibility of the experiments. Interestingly, a selectivity of 52 ± 5.2 % was found, which was in the similar range to the value obtained with Ru/C.
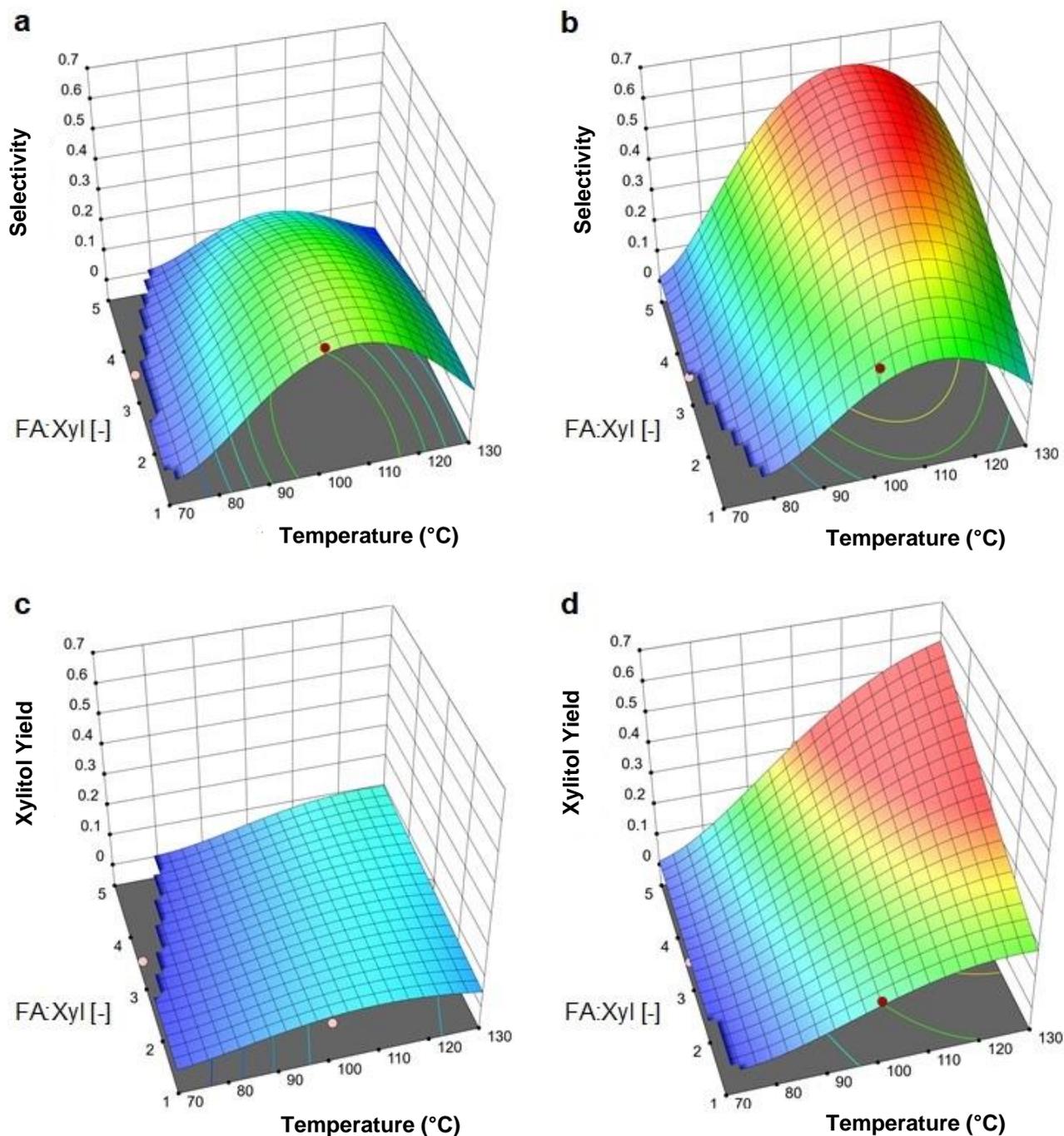

Fig. 4. Response surfaces after DoE using Ru/Al$_2$O$_3$ as a catalyst. Selectivity and xylitol yield in dependence of Et$_3$N concentration are shown. Figures (a) and (c) illustrate selectivity and xylitol yield without the addition of Et$_3$N, figures (b) and (d) show the results with a Et$_3$N:FA ratio of 0.4.

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Table 6. Parameters of the Experimental Runs and the Resulting Response Values for the CTH with Ru/Al$_2$O$_3$

	Factors			Response	
Run	A (°C)	B (-)	C (-)	Y(D-xylitol)	S(D-xylitol)
1	130	5	0.2	0.362	0.362
2	130	1	0.2	0.122	0.136
3	100	3	0.2	0.147	0.522
4	100	1	0	0.056	0.355
5	130	3	0	0.075	0.089
6	100	5	0	0.024	0.081
7	100	1	0.4	0.136	0.295
8	100	3	0.2	0.153	0.462
9	70	3	0	0	0
10	70	3	0.4	0	0
11	70	5	0.2	0	0
12	70	1	0.2	0	0
13	100	3	0.2	0.169	0.564
14	130	3	0.4	0.319	0.319
15	100	5	0.4	0.321	0.534
A: temperature; B: *Xyl/FA* ratio; C: *Et$_3$N/FA* ratio					

Table 7. Analysis of Variance (ANOVA) for Quadratic Model with Arcsin Transformation for Ru/Al$_2$O$_3$ Catalyst

Parameter	Sum of squares	df	Mean square	F-value	p-value
Y(Xylitol)					
Model	0.707	7	0.101	31.67	< 0.0001
A-Temperature	0.433	1	0.433	135.92	< 0.0001
B-FA:Xyl	0.006	1	0.006	1.82	0.2191
C-Base:FA	0.049	1	0.049	15.39	0.0057
AB	0.021	1	0.021	6.53	0.0378
AC	0.026	1	0.026	8.2	0.0242
BC	0.024	1	0.024	7.51	0.0289
A²	0.069	1	0.069	21.53	0.0024
Residual	0.022	7	0.003		
Lack of Fit	0.022	5	0.004	18.39	0.0524
Pure Error	0.001	2	0.000		
Cor Total	0.729	14			
S(Xylitol)					
Model	1.42	7	0.180	23.45	0.0006
A-Temperature	1.19	1	1.19	155.27	< 0.0001
B-FA:Xyl	0.003	1	0.003	0.4341	0.5344
C-Base:FA	0.033	1	0.033	4.26	0.0846
AC	0.022	1	0.022	2.87	0.1413
BC	0.088	1	0.088	11.51	0.0146
A²	0.747	1	0.747	97.4	< 0.0001
B²	0.034	1	0.034	4.41	0.0806
C²	0.058	1	0.058	7.58	0.0331
Residual	0.046	6	0.008		
Lack of Fit	0.041	4	0.010	3.81	0.2188
Pure Error	0.005	2	0.003		
Cor Total	1.49	14			

Table 8. Results of the Statistical Analysis for the DoE with Ru/Al$_2$O$_3$ Catalyst

Parameter	Response	
	Y(Xylitol)	*S(Xylitol)*
Std. Dev.	0.0565	0.0986
Mean	0.2981	0.4433
C.V. (%)	18.94	22.24
R²	0.9694	0.9542
Adjusted R²	0.9388	0.9084
Predicted R²	0.8077	0.7384
Adeq Precision	16.8938	13.2601

The D-xylitol yield and selectivity may be calculated using following equations:

$$ArcSin\sqrt{Y(Xylitol)}$$
$$= 1.367 + 0.032 \times A - 0.032 \times B - 1.360 \times C + 0.001 \times AB + 0.013 * AC + 0.193 \times BC - 0.0002 + A^2$$

$$ArcSin\sqrt{S(Xylitol)}$$
$$= -5.244 + 0.108 \times A - 0.079 \times B - 0.618 \times C + 0.371 \times BC - 0.0005 * A^2 - 0.024 \times B^2 - 3.139 \times C^2$$

The statistical analysis of variance (ANOVA) is shown in Table 7 and Table 8. Again, the evaluation of the responses *Y(Xylitol)* and *S(Xylitol)* resulted in a significant model and a non-significant Lack of Fit value. In case of *Y*, the significant model terms were A, B, C, AB, AC, BC and A², whereas A, B, C, AC, BC, A², B² and C² turned out to be significant for *S*.

High reliability of the relationship between predicted and experimentally determined values was attested, as the difference between the predicted and the adjusted R^2 value was < 0.2. C.V. (coefficient of variation) of *S(Xylitol)* and *Y(Xylitol)* were of similar magnitude, indicating comparable data accuracy and validity. A signal to noise ratio (Adeq. Precision) by far exceeded the minimum value of 4.

In summary, the results of the DoE experiments provide a good overview of various influencing factors on the CTH conversion from D-xylose to D-xylitol with a consistently good reproducibility and correspondence between the measuring point and the model. The tested factors temperature, formic acid/D-xylose ratio and triethylamine/formic acid ratio had a significant influence on the reaction. In particular, the experiments without triethylamine resulted in a rather low level of xylitol yield, confirming the necessity of a base addition, regardless the catalyst used. According to literature, the addition of basic components results in increased selectivity, improved reaction kinetics and reduced catalyst deactivation (Nie *et al.* 2021). Further, the use of high amounts of the H donor may be derived after data evaluation, however too acidic conditions may as well affect catalyst stability (leaching) or even lead to its deactivation, or result in high amount of undesired side products.

Xylose Loss Reactions

During the optimization experiment, D-xylose conversion increased with increasing temperature and the amount of formic acid as well as with enhanced concentration of triethylamine. In some runs xylose was completely consumed, but at the same time, the yields of xylitol were far from reaching the maximum. Therefore, a more detailed analysis

of the residual liquors of the experiments with the highest D-xylitol yields was performed for both catalysts (Table 9). There was no residual xylose found in the final reaction medium. However, only 73% (Ru/C) and 36% xylitol yield (Ru/Al$_2$O$_3$) was detected respectively, indicating dissimilarly pronounced by-product formation. In case of Ru/C, xylonic acid made up the remaining 27 % of the products. Xylose itself may act as an H-donor, resulting in disproportionation into xylitol and xylonic acid (Mikkola *et al*. 2000). Preferably, this reaction route should be avoided, as it leads to considerable xylitol yield loss.

The use of Ru/Al$_2$O$_3$ as a catalyst resulted in significantly lower xylonic acid formation (6%), but also in half the xylitol yield compared to Ru/C. The 57% of the reaction products remained unidentified. Low pH values favor dehydration of D-xylose to furfural, which can be further hydrogenated to furfuryl alcohol and tetrahydrofuryl alcohol. However, none of these was determined in the solution. Further, the solutions were tested negative for the presence of levulinic acid, which may be formed as a furfuryl alcohol degradation product.

Table 9. Composition of the Product Solutions with the Highest Xylitol Yields after the CTH of Xylose with Formic Acid

Catalyst	Xylitol (%)	Xylonic acid (%)	Furans (%)	Unidentified (%)
Ru/Al$_2$O$_3$	36	6	0	57
Ru/C	73	27	0	0

The relatively harsh reaction conditions led to complex sugar and furan degradation and high molar mass polymerization products. The identification of the entity of degradation products would require time-consuming method development, which was not possible within the current project. However, in future, such studies may contribute to a more detailed understanding of the reactions.

When comparing both catalysts, Ru/C seemed to be highly active in forming metal hydride species. This high activity on the contrary led to the formation of xylonic acid *via* H-donation from xylose. The Ru/Al$_2$O$_3$ catalyst on the other hand showed less activity, thus leading to sugar degradation and low yields. Based on literature concerning Ru catalysts on alternating support materials, it is speculated that this difference is caused by the chemical nature and the morphology of the carrier, as it interacts with the metallic Ru (Vilcocq *et al*. 2021). Due to its amphoteric character, Al$_2$O$_3$ may interact with the species involved in the hydrogenation, changing the reaction rate and the overall reaction yield. The role of the catalyst support was confirmed in studies on hydrogenation reaction systems (Filonenko *et al.* 2016). König *et al.* (2014) described the different catalyst inactivation by sulphur containing components in dependence of the support properties. One should keep that in mind, especially when processing pulping derived streams, as sulphur is omnipresent in that field.

Generally, catalytic transfer hydrogenation with external H donors is a chemically efficient, environmentally friendly alternative to conventional hydrogenation. The process avoids several serious drawbacks associated with the use of hydrogen gas. CTH has attracted interest due to its advantageous properties, such as achieving high atomic yields under mild reaction conditions, lower energy intensity, and the use of H donors from renewable sources. Although yields are low compared to conventional hydrogenation of xylose, it must be pointed out that this is the first report on the CTH of xylose using formic

acid. On the contrary, xylitol production using H_2 is done at industrial scale for decades and has been extensively optimized during this period. Thus, it is speculated that CTH yields will increase with future investigation, *e.g.* due to catalyst development.

Using formic acid as a hydrogen source results in an inevitable release of CO_2. It may be recycled to formic acid by hydrogenation; however, when fossil-based H_2 is used, the advantage of formic acid diminishes compared to direct hydrogenation. On the other hand, the resulting CO_2 is pure and may be easily removed. It may be directly used in CO_2 binding reactions or as a supercritical solvent, as the technology has been gaining attention in recent years (Munshi and Bhaduri 2010; Liu *et al.* 2015; Liu *et al.* 2022). Xylose and formic acid may be obtained as side-streams of biomass processing, e.g. kraft pulp production, and the processing to an attractive and valuable-added co-product would push pulp mills further towards wood biorefinery.

To live up to the idea of sustainability, a few words should be said on the recycling of additives and catalyst. The amine base is not consumed during CTH and thus needs to be separated from the product solution and recycled back to the process. Due to the large differences in physical properties compared to xylitol, this can be easily done, *e.g.* by distillation or liquid-liquid extraction. The catalyst remains solid during the reaction and may be easily recovered by filtration and reused. Literature describes poisoning of Ru with Cl, CO, and N-containing aromatics; however, they present less of a problem in the environment of a pulp mill. Sulphur was found to interact with the catalyst support, especially when activated carbon is used, resulting in diminished reactivation ability (König *et al.* 2014). That may be challenging, due to the presence of sulfur compounds in pulp production sites. In order to determine the maximum catalyst lifetime, the investigation of sensitivity to leaching and the additives under CTH conditions would be beneficial, especially when using components originating from a kraft mill.

Nevertheless, the best practice for producing xylitol is to use educts in highest possible purity, as the separation of the various co-products from xylitol may be challenging, compared to the established xylose separation techniques. Due to the fact that xylitol has been an established product for decades, numerous established purification methods may be applied, depending on the production process and the resulting concentration (Martínez *et al.* 2015). Crystallisation is a widely used xylitol purification method. By adjusting the crystallization parameters to the particular product composition, various impurities can be efficiently removed.

CONCLUSIONS

1. The production of xylitol *via* catalytical transfer hydrogenation of xylose, a sugar derived from lignocellulosic biomass, was shown to be feasible. The employment of formic acid as a bio-based H-donor improves the process sustainability.

2. Xylitol yield was significantly increased by the addition of triethylamine, due to the enhanced H-donor activity of the formate.

3. The catalysts Ru/C (Thermo scientific) and Ru/Al_2O_3 (Heraeus) showed the best performance in the preliminary tests and led to effective maximum xylitol yields of 73% and 36% under optimized conditions

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SUPPLEMENTARY

APPENDIX

Table S1. Parameters of the Experimental Runs and the Resulting Response Values for the Xylose Conversion with Both Catalysts

	Factors			Response $X(Xylose)$	
Run	A (°C)	B (-)	C (-)	Al_2O_3	Ru/C
1	130	5	0.2	1	1
2	130	1	0.2	0.900	0.816
3	100	3	0.2	0.315	1
4	100	1	0	0.191	0.121
5	130	3	0	0.84	0.443
6	100	5	0	0.316	0.084
7	100	1	0.4	0.449	0.797
8	100	3	0.2	0.317	1
9	70	3	0	0	0.018
10	70	3	0.4	0	0.039
11	70	5	0.2	0	0
12	70	1	0.2	0	0.034
13	100	3	0.2	0.338	1
14	130	3	0.4	1	1
15	100	5	0.4	0.621	1
A: temperature; B: Xyl/FA ratio; C: Et_3N/FA ratio					

Table S2. Analysis of Variance (Anova) of Xylose Conversion for Quadratic Model with Arcsin Transformation for Ru/Al_2O_3 Catalyst

Parameter	Sum of squares	df	Mean square	F-value	p-Value
$X(Xylose)$					
Model	4.11	7	0.587	597.52	< 0.0001
A-Temperature	1.77	1	1.77	1798.38	< 0.0001
B-FA:Xyl	0.018	1	0.018	18.13	0.0038
C-Base:FA	0.053	1	0.053	54.07	0.0002
AB	0.026	1	0.026	26.41	0.0013
AC	0.042	1	0.042	43.1	0.0003
A²	0.011	1	0.011	11.22	0.0123
B²	0.007	1	0.007	6.76	0.0354
Residual	0.007	7	0.001		
Lack of Fit	0.007	5	0.001	7.53	0.1214
Pure Error	0.000	2	0.000		
Cor Total	4.12	14			

Table S3. Results of the Statistical Analysis for the DoE with Ru/Al_2O_3 Catalyst

Parameter	Response
	$X(Xylose)$
Std. Dev.	0.0313
Mean	0.6697
C.V. (%)	4.68
R²	0.9983
Adjusted R²	0.9967

Predicted R²	0.9884
Adeq Precision	71.4854

Table S4. Analysis of Variance (ANOVA) of Xylose Conversion for Quadratic Model with Arcsin Transformation for Ru/C Catalyst

Parameter	Sum of squares	df	Mean square	F-value	p-Value
X(Xylose)					
Model	5.68	9	0.632	16.04	0.0035
A-Temperature	2.51	1	1.77	1798.38	0.0005
B-FA:Xyl	0.055	1	0.055	1.39	0.2914
C-Base:FA	1.07	1	1.07	27.27	0.0034
AB	0.099	1	0.099	2.51	0.174
AC	0.152	1	0.152	3.85	0.1071
BC	0.070	1	0.070	1.78	0.2395
A²	0.964	1	0.964	24.49	0.0043
B²	0.423	1	0.423	10.75	0.022
C²	0.594	1	0.594	15.09	0.0116
Residual	0.197	5	0.039		
Lack of Fit	0.197	3	0.066		
Pure Error	0	2	0		
Cor Total	5.88	14			

Table S5. Results of the Statistical Analysis for the DoE with Ru/C Catalyst

Parameter	Response
	X(Xylose)
Std. Dev.	0.1984
Mean	0.9037
C.V. (%)	21.96
R²	0.9665
Adjusted R²	0.9063
Predicted R²	0.4644
Adeq Precision	11.4309